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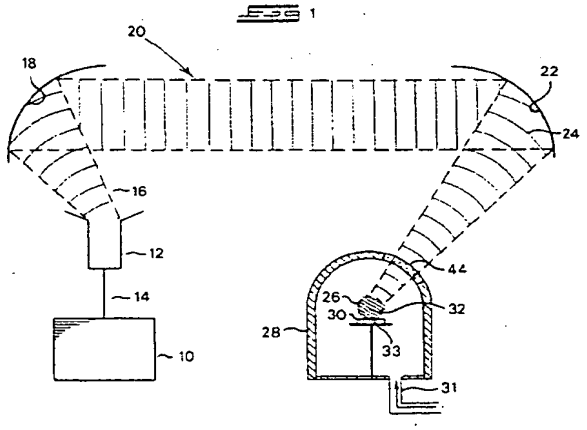
(54) Plasma assisted diamond synthesis.

(57) The invention relates to a method of forming a plasma (32) for assisting in the production of a ceramic material such as diamond (33). The method includes the steps of providing a bell jar (28), and introducing a selected gas into the bell jar. The gas may comprise an active gas such as hydrogen, and a gaseous carbon compound. A beam of microwave radiation (16) is generated from a remote source (10), and is focused using an array of lenses or mirrors (18, 22) to a focal region (26) within the reaction chamber so as to form a plasma (32) in this region. The shape of the plasma is independent of the inner profile of the chamber and dependent on the geometry and position of the focusing array. A substrate (30) is located within the reaction chamber, and the plasma interacts with the substrate so as to cause chemical vapour deposition of, for instance, a plasma activated carbon component of the plasma onto the substrate. The invention extends to apparatus for use in the method.



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BACKGROUND TO THE INVENTION

This invention relates to the synthesis of diamond and other ceramic materials using a plasma assisted chemical vapour deposition (CVD) technique.

Diamonds have been produced synthetically for the past three or so decades by subjecting a carbon source such as graphite to a pressure exceeding 50 kilobars and a temperature exceeding 1200°C in the presence of a catalyst metal such as nickel, cobalt or iron. More recently, diamonds have been synthesised from the gas phase. This method is known as chemical vapour deposition (CVD) and the diamond produced is known as CVD diamond. The process generally involves providing a mixture of hydrogen gas and a suitable gaseous carbon compound such as a hydrocarbon, applying sufficient energy to that gas to dissociate the hydrogen into atomic hydrogen and the gas into active carbon ions, atoms or CH radicals and allowing such active species to deposit on a substrate to form diamond. Dissociation of the gases can take place by a variety of methods.

One such method is the use of a hot filament to dissociate the gases in the region around the filament. A second commonly used method is a plasma assisted method. The hydrogen and gaseous carbon compound enter a plasma region, which may be microwave-,RF-or DC- formed plasma, where they are excited to their active states. They diffuse in this state onto a substrate, which is heated by the plasma. Microwave plasma assisted CVD has, in the past, used waveguides to generate the plasma inside a reaction chamber contained within the waveguide. The intense electric field generated within the confines of the waveguide, or the waveguide cavity, is sufficient to ionise the low pressure gasses contained within the reaction chamber. The plasma thus generated deposits diamond onto a substrate placed in the plasma, or adjacent thereto.

A disadvantage of the use of a waveguide to form a plasma is that the size of the plasma is determined by the dimensions of the waveguide enclosure. An increase in the size of the plasma cannot merely be effected by increasing the size of a waveguide, as, without a proportional increase in microwave wavelength, multi-mode propagation occurs. This results in the inefficient generation of plasma.

As the plasma is confined to the electric field lines present within the waveguide, its position is static within the reaction chamber. This presents additional problems. Firstly, the insertion of a substrate into the waveguide disrupts the electric field lines in an unpredictable manner, which is dependent upon the nature and the geometry of the substrate. Secondly, the plasma can come into contact with the walls of the reaction chamber that are unavoidably within the confines of the waveguide. This can lead to contamination of the diamond deposit on the substrate.

SUMMARY OF THE INVENTION

According to a first aspect of the invention there is provided a method of forming a plasma comprising the steps of:

i. providing a reaction chamber;

ii introducing a selected gas into the reaction chamber;

iii generating a beam of microwave radiation from a remote source;

iv focusing the microwave radiation to a focal region within the reaction chamber so as to form a plasma in the focal region, the shape of the plasma being independent of the internal profile reaction chamber.

Preferably, the method includes the steps of providing a substrate within the reaction chamber and allowing the plasma to interact with the substrate to cause chemical vapour deposition of plasma-activated species onto the substrate.

According to a second aspect of the invention there is provided a method of forming a plasma for assisting in the production of a ceramic material by chemical vapour deposition including the steps of:

i defining a plasma forming zone;

ii introducing a selected gas into the plasma forming zone;

iii generating a beam of microwave radiation at a remote source;

iv focusing the beam of microwave radiation from remotely positioned focusing means onto the plasma forming zone, so as to form a plasma, the shape and position of the plasma being dependent on the geometry and positioning of the focusing means.

The selected gas preferably includes a precursor gas mixture and an active gas chosen from the group comprising hydrogen and oxygen, and the precursor gas mixture may include a gaseous carbon compound for the chemical vapour deposition of diamond.

Conveniently, the method includes the step of providing a substrate and scanning the plasma over the substrate by adjusting the position of the focusing means and the substrate relative to one another.

According to a still further aspect of the invention, there is provided a method of forming a plasma for assisting in the production of diamond by chemical vapour deposition includes the steps of:

i. providing a reaction chamber;

ii locating a substrate within the reaction chamber;

iii providing an external source of microwave radiation;

iv introducing a mixture of a gaseous carbon compound and an active gas chosen from the group including hydrogen and oxygen into the reaction chamber, and

v focusing the microwave radiation to a focal point

a plasma within the reaction chamber in
n of the substrate, so as to cause chem-
ur deposition of diamond onto the sub-

ntion extends to an apparatus for form-
a, the apparatus comprising a reaction
using means for focusing a beam of mi-
ation from a remote source to a focal re-
e reaction chamber, and means for intro-
ected gas into the chamber, the focusing
arranged to form a plasma in the focal

pe of the plasma is preferably indepen-
ner profile of the reaction chamber and
n the geometry and positioning of the fo-
s.
geously, the apparatus includes a sub-
d within the reaction chamber adjacent
wherein interaction of the plasma and the
sults in the chemical vapour deposition of
ated species onto the substrate.
using means may comprise at least one
ing a concave reflective surface dimen-
at least four times the wavelength of the
adiation.
ecifically, the focusing means may com-
d second parabolic reflectors, the first re-
arranged to receive a beam of micro-
on from a microwave generator and to
beam to the second reflector, which is ar-
cus the beam.
ans for introducing the selected gas may
cuum pump for evacuating the reaction
pressurized source of the selected gas
ing with the reaction chamber, and valve
ontrolling the supply of the selected gas
on chamber.
ntion is not limited to the formation of di-
chemical vapour deposition. Numerous
ic materials, including Si, GaS, InP, ZnS,
SiC, and cubic boron nitride may be
using a suitable precursor gas mixture.
may also be used in the etching and sur-
ation of material. For example, it may be
emoval of oxide layers prior to brazing, or
in the reflow of brazes and solders.
erm microwave radiation, for the purpos-
ecification, it is meant that the radiation
ible frequency range from 300MHz to
preferably from 433MHz to 94GHz, and
ably in the region between 2GHz and

CRIPTION OF THE DRAWINGS

I shows a highly schematic view of a first
ment of plasma forming apparatus of the
n;

Figures 2 to 5 show schematic views of further embodiments of plasma forming apparatus of the invention in which various focusing arrangements are employed, and

Figures 6 and 7 show schematic views of an experimental arrangement for creating a suitable plasma.

DESCRIPTION OF EMBODIMENTS

Referring now to Figure 1, a microwave generator 10 powers a radiating horn 12 via a suitable waveguide 14. The horn 12 is positioned to radiate a beam 16 of microwave radiation onto a first curved parabolic reflector 18. The reflector 18 has a suitable reflecting surface geometry in order to enable the incoming beam 16 to be reflected as a parallel plane wave 20 through free space. The plane wave train 20 is collected by a second reflector 22, which has a substantially parabolic reflecting surface for transforming the plane wave train 20 into a convergent spherical wave train 24. The convergent spherical wave train 24 converges to a focal point or region 26 which is located within a reaction chamber 28, such as a bell jar, which defines a plasma-forming zone 29.

Housed within the reaction chamber 28 towards the centre thereof is a suitable substrate 30 such as silicon carbide, molybdenum, silicon or even a diamond seed. It is clear from the drawing that the substrate 30 is positioned just beneath the focal point 26.

A carbon containing gas is combined with hydrogen, oxygen, argon, helium, neon, water vapour, or any functioned combination thereof, and is introduced into the reaction chamber 28 via an inlet pipe 31 at a pressure of between 0,1 and 700 Torr, and preferably from 40 to 200 Torr. If sufficient power, in excess of $1Wcm^{-3}$, is concentrated within the focal region 26, then a plasma 32 is generated in the low pressure gases contained within the reaction chamber 28. As is schematically illustrated, the plasma 32 is concentrated at the focal point 26 of the second reflector 24. The substrate is heated by the hot plasma gases to a temperature of between 400K and 1500K. This temperature is usually in the region of 900K. Diamond deposition (33) occurs on the substrate 30, in a manner similar to that described in US Patent 4434188 to Kamo.

In contrast to prior art reaction chambers, which are limited by the size of the waveguide cavity within which they are confined, the size of the reaction chamber 28 is not limited by any waveguide dimensions. As a result, the substrate 30 may be placed well away from the walls of the reaction chamber and other sources of contamination. Furthermore, as there are no cavity nodes within the reaction chamber, the insertion of a substrate has little, if any affect on the position of the plasma discharge 32. Similarly, the nature and geometry of the substrate 30 has negligible

effect on the plasma discharge 32.

Referring now to Figure 2, a further embodiment is shown in which a lens 34 replaces the second mirror 22 of Figure 1 as a means of focusing the microwave radiation. In Figure 3, a single bi-convex lens 36 replaces both the first reflector 18 and the second reflector 22. The lens may be a dielectric lens, a metal plate lens or a fresnel zone plate lens. The arrangement illustrated in Figure 4 utilises a single reflector 38 in place of the lens 36. In Figure 5, a lens 40 is used to collimate the beam of microwave radiation, and a reflector 42 focuses the collimated beam. It should be appreciated that various combinations of lenses and reflectors may be used to focus the beam of microwave radiation, which may be continuous, pulsed, modulated or polarized, or a combination of these. For instance, an ellipsoid having a reflective inner surface may be used, with the microwave source and the plasma being located at the two respective focal points within the ellipsoid.

An advantage of the various focusing systems employed is that they may be used to obtain different plasma shapes by altering the profiles of the focusing lens or the reflector. For example, a roughly spheroidal plasma can be obtained by using a reflector that has a paraboloid reflecting surface. A bi-convex lens may also be used to achieve a similar spheroidal plasma. An elongate linear plasma may be obtained by means of a parabolic reflecting surface which is in the form of a section of a parabolic cylinder, or by a spherical reflecting surface. Further plasma shapes, as well as plasma density profiles, may be obtained by subtle variation in the microwave optics.

It is also possible to change the size and position of the plasma by adjusting the focal length of the focusing optics and by moving the final focusing device along or around its central axis of symmetry.

Scanning of the plasma in three dimensions may also be achieved by movement of the final focusing optics or of the substrate within the reaction chamber in a suitable manner. Three-dimensional surfaces may be coated with diamond by simply scanning the plasma over the entire surface of the substrate.

Several radiating horns could also be used to illuminate the first reflector or the first lens. At least two frequencies could thus be coupled within the plasma, which could, for example, be advantageously used in the selective excitation of specific species within the plasma. Similarly, two polarisation directions could be combined in differing ratios to make possible further refinements to the plasma discharge.

In a further embodiment of the invention, very high microwave frequencies could be focused to an extremely small diffraction limited spot having a diameter of approximately half the wavelength of the incoming microwave radiation, thereby enabling tiny, localised plasmas to be created. Such plasmas could then be scanned over a substrate surface in the manner described previously in the specification, in order to enable diamond to be "written" onto the substrate.

In order to minimise edge effects and to give efficient illumination of the optics, the microwave optics typically need to be large (i.e. at least four times, and preferably at least ten times) the microwave wavelength. Potentially hazardous radiation may be eliminated by enclosing the optics either in a metallic screen or by means of a suitable absorbing material.

The reaction chamber 28 should either be transparent in its entirety, or could alternatively be provided with a transparent window 44 which must be in the form of a dielectric, in order to be transparent to the microwave radiation. A further possibility is for the reaction chamber to be of such a size that it encloses both the focusing arrangement and the substrate. Preferable materials for the entire reaction chamber or for the window 44 are fused silica, quartz, zirconia, alumina, pyrex, PTFE, Macor®, silica glass or polystyrene. These materials could be coated with an anti-reflection medium in order to minimise reflection losses from the surfaces. The materials may also be cooled by means of a suitable transparent fluid such as cyclohexane.

EXAMPLE

A prototype system was outdoors comprising a microwave generator, an arrangement of focusing microwave dishes and a reaction chamber in the form of a quartz bell jar. A plasma of several centimetres across was successfully generated in space using a microwave generator having a power of only 800 watts.

Referring to Figure 6, a pair of offset parabolic reflectors 44 and 46 were manufactured from wooden ribs with a stainless steel mesh stretched across the ribs. Parabolic templates were used to check the surface accuracy of the reflectors 44 and 46 to within ± 2mm (one sixtieth of a wavelength), which was well within typical permissible tolerances. The leakage through the mesh was calculated to be -20dB(1%). The reflectors each had a cross-sectional dimension of 1.5m, or twelve wavelengths. The focal length of each reflector was fixed at 1.5m. An antenna horn 48 having 10dB beam widths of 42° in the E-plane and 59° in H-plane was positioned just rearwardly of the focal point 50 of the reflector 44. The azimuth subtended angle of the reflector was approximately 56° and the elevations subtended angle of the reflector was 44°, resulting a relatively good match between the horn 48 and the reflector 44, provided that the horn was mounted with its E-plane vertical.

The second parabolic reflector 46 was located with its focal point 52 being approximately two meters away from the focal point 50 of the reflector 44. A magnetron transmitter 54 having a frequency of operation of 2.45GHz and an output power of approximately 1.6

kW was arranged to feed the horn 48. The peak power density of the horn aperture was calculated as being 54kW m^{-2}. At a distance of 1.5m, which represented the distance between the aperture of the horn 48 and the reflector 44, the power density dropped to a calculated value of 3.15kWm^{-2}. Owing to the arrangement of reflectors 44 and 46, it was calculated that most of the microwave radiation reflected from the reflector 44 would be captured by the reflector 46.

The reflector 44 was mounted on a fixed structure, and the reflector 46 was mounted on a trolley which ran along a track. A horn 56 and a power meter 58 were positioned adjacent the focal point 52 of the removable reflector 46, and the magnetron transmitter 54 was replaced by low power transmitter. The final positions of the reflectors 44 and 46 are indicated in Figure 6, with the respective foci 50 and 52 of the reflectors being 2.08m apart. The measured loss between the reflectors 44 and 46 was approximately 2.7dB. This was higher than expected, which was probably due to spillover at the edges of the reflectors 44 and 46 as well as a higher mesh leakage than had been calculated. The horn 48 was then connected to the magnetron transmitter 54, which was water-cooled, and driven from a remote power supply. The horn 56 was removed and the field region of the focal point 52 was probed using a neon discharge tube suspended by a fine cotton thread. The neon discharge tube struck in the region having a diameter of between 5 and 8 centimetres. The position of maximum power was also located by using a block of absorbent foam covered in heat sensitive paper.

An arrangement similar to that indicated in Figure 6 was then provided, with the horn 56 being replaced by a quartz bell jar 62. The bell jar 62 was mounted on the movable platform 64, and a thin wire dipole 66 about 1.5mm in diameter and 60mm in length was placed on a piece of low loss foam 68 within the bell jar 62. The bell jar 62 was then evacuated by being brought down to 0.1 Torr by means of a vacuum pump 70 via a pipe 72. A pressure indicator 74 indicated the reduction in pressure in the pipe 72, and a valve 76 was closed once the required pressure had been attained as indicated by the gauge 77. A valve 78 was then opened, causing the bell jar 62 to be filled from a source of argon 80 via a pipe 82. Once the pressure within the bell jar 62 reached 1.0 Torr, the valve 76 was then opened and the pump 70 was then operated to evacuate the jar 62 back down to 0.1 Torr. The jar 62 was then sealed, and the magnetron transmitter 54 was then activated, causing a focused beam of microwave radiation in the region of the dipole 66 to form a plasma of approximately five to eight centimetres in diameter.

The argon was subsequently replaced by a mixture of H_2 and CH_4 gas in a volume ratio of 100:1. This gas mixture was passed continuously through the bell jar at a rate of 200 sccmin. A silicon carbide substrate approximately 5mm square replaced the foam 68 and the dipole 66. The pressure within the bell jar was maintained at 40 Torr, and the magnetron transmitter was then activated, causing a plasma to form adjacent the substrate. This plasma caused the substrate to attain a temperature of 1170 K, maintained by cooling. This resulted in a layer of diamond forming on the substrate by chemical vapour deposition at an observed growth rate of 1 μm per hour.

Claims

1. A method of forming a plasma (32) characterized in that its comprises the steps of:
   i providing a reaction chamber (28);
   ii introducing a selected gas into the reaction chamber;
   iii generating a beam (16) of microwave radiation from a remote source (10);
   iv focusing the microwave radiation to a focal region (26) within the reaction chamber (28) so as to form a plasma (32) in the focal region, the shape of the plasma (32) being independent of the internal profile of the reaction chamber (28).

2. A method according to claim 1 characterized in that it includes the steps of providing a substrate (30) within the reaction chamber (26) and allowing the plasma to interact with the substrate (30) to cause chemical vapour deposition of components of the plasma onto the substrate (30).

3. A method of forming a plasma for assisting in the production of a ceramic material by chemical vapour deposition characterized in that it includes the steps of:
   i defining a plasma forming zone (29);
   ii introducing a selected gas into the plasma forming zone;
   iii generating a beam of microwave radiation (16) at a remote source (10);
   iv focusing the beam of microwave radiation from remotely positioned focusing means (18, 22) onto a focal region (26) within the plasma forming zone so as to form a plasma (32), the shape and position of the plasma being dependent on the geometry and positioning of the focusing means.

4. A method of forming a plasma according to any one of the preceding claims characterized in that the selected gas includes a precursor gas mixture and an active gas chosen from the group comprising hydrogen and oxygen.

5. A method according to claim 4 characterized in

that the precursor gas mixture includes a gaseous carbon compound for the chemical vapour deposition of diamond.

6. A method according to claim 3 which includes the step of providing a substrate (30) and scanning the plasma (32) over the substrate by adjusting the position of the focusing means (22) and the substrate (30) relative to one another.

7. A method of forming a plasma for assisting in the production of diamond by chemical vapour deposition characterized in that it includes the steps of:
   i. providing a reaction chamber (28);
   ii locating a substrate (30) within the reaction chamber;
   iii providing an external source of microwave radiation (10);
   iv introducing a mixture of gaseous carbon compound and an active gas chosen from the group including hydrogen and oxygen into the reaction chamber (28), and
   v focusing the microwave radiation (24) to a focal point (26) to form a plasma within the reaction chamber in the region of the substrate, so as to cause chemical vapour deposition of diamond (33) onto the substrate.

8. An apparatus for forming a plasma characterized in that it comprises a reaction chamber (28), focusing means (18, 22; 34; 36; 38; 40, 42) for focusing a beam of microwave radiation (16) from a remote source (10) to a focal region within the reaction chamber, and means (78, 80, 82) for introducing a selected gas into the chamber, the focusing means being arranged to form a plasma (32) in the focal region (26).

9. An apparatus according to claim 8 characterized in that the shape of the plasma (32) is independent of the shape of the reaction chamber (28) and dependent on the geometry and positioning of the focusing means (18, 22).

10. An apparatus according to either one of claims 8 or 9 characterized in that it includes a substrate (30) located within the reaction chamber (28) adjacent the plasma (32), wherein interaction of the plasma and the substrate results in the chemical vapour deposition of plasma-activated species (33) onto the substrate.

11. An apparatus according to any one of claims 8 to 10 characterized in that the focusing means comprises at least one reflector (18, 22, 44, 46) having a concave reflective surface dimensioned to be at least four times the wavelength of the microwave radiation.

12. An apparatus according to claim 11 characterized in that the focusing means comprises first and second parabolic reflectors (18, 44; 22, 46), the first reflector (18, 44) being arranged to receive a beam of microwave radiation (16) from a microwave generator (10) and to transmit the beam (20) to the second reflector (22, 46), which is arranged to focus the beam.

13. An apparatus according to claim 12 characterized in that the second parabolic reflector (22, 46) and the substrate (30) are adjustable relative to one another so as to scan the plasma over the substrate.

14. An apparatus according to any one of claims 8 to 13 characterized in that the means for introducing the selected gas includes a vacuum pump (70) for evacuating the reaction chamber, a pressurized source of the selected gas (80) communicating with the reaction chamber, and valve means (78) for controlling the supply of the selected gas to the reaction chamber.

FIG 1

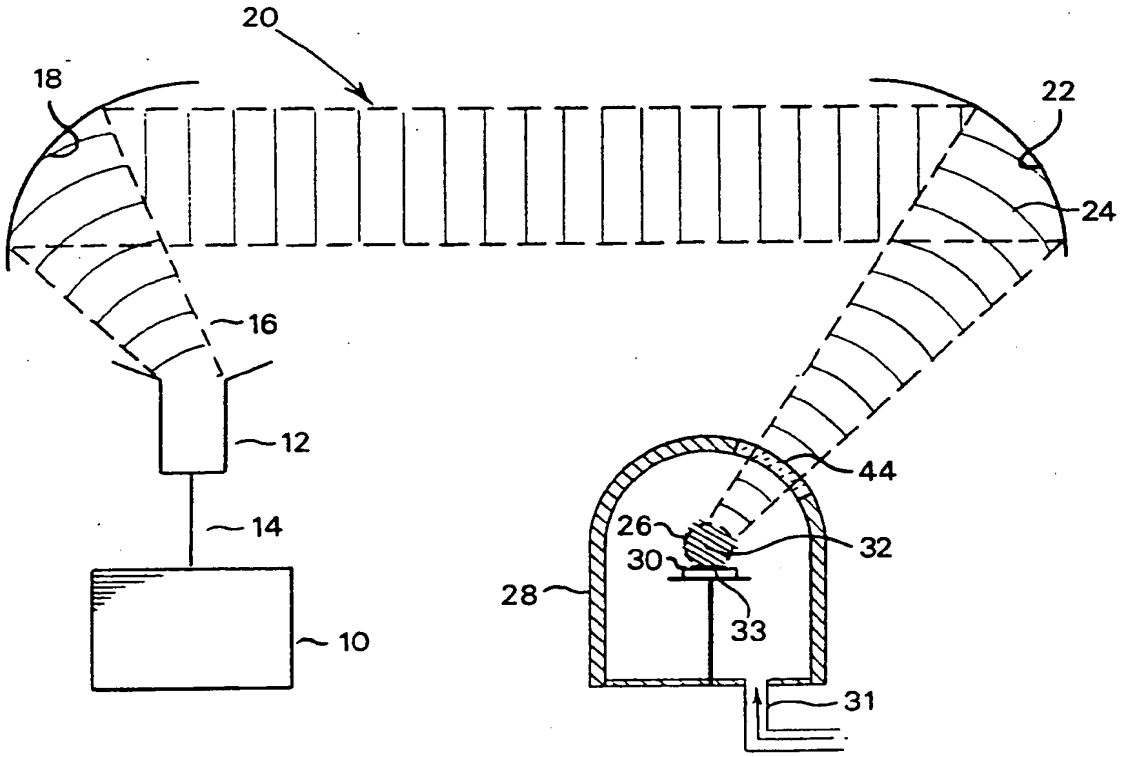


FIG 2

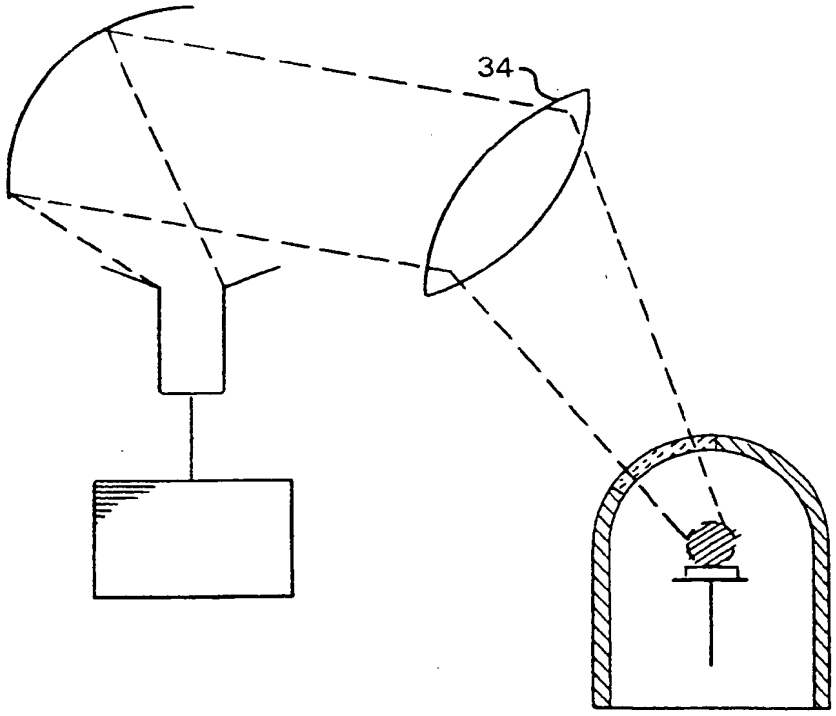


FIG 3

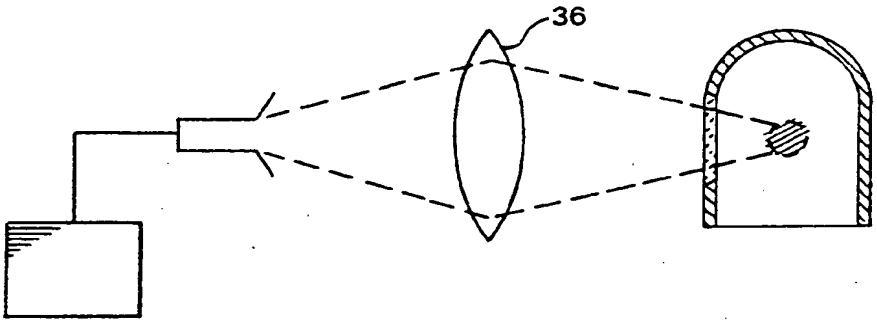


FIG 4

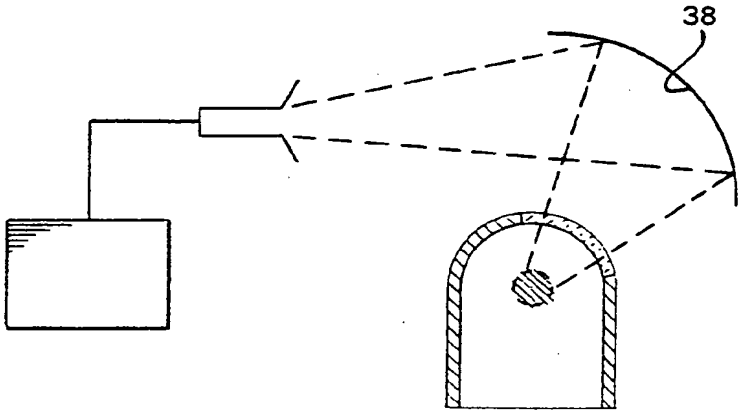


FIG 5

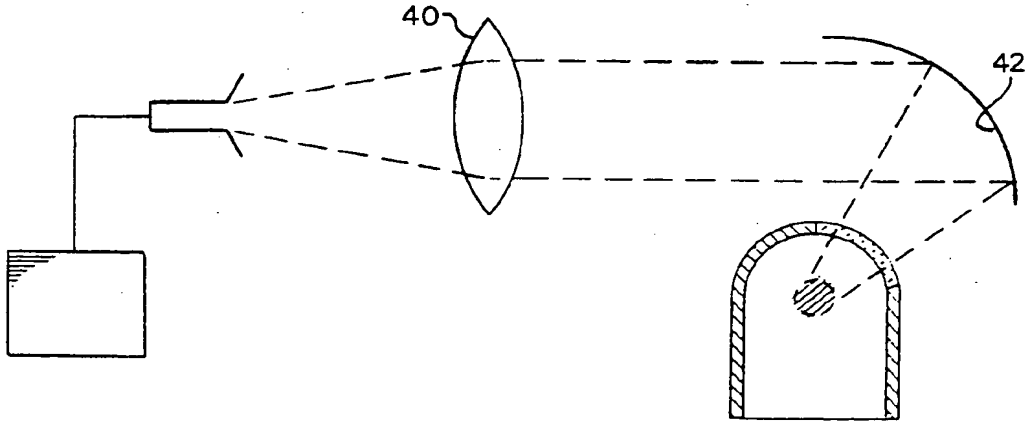


Fig. 6

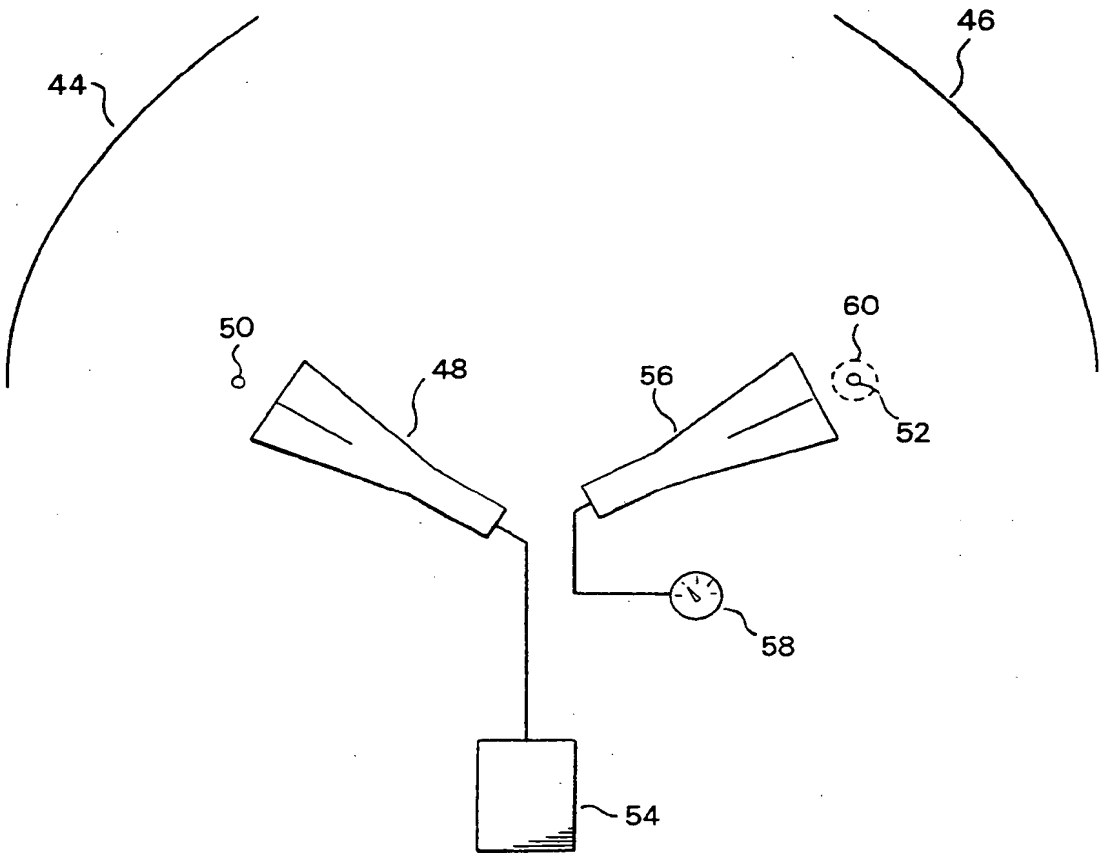
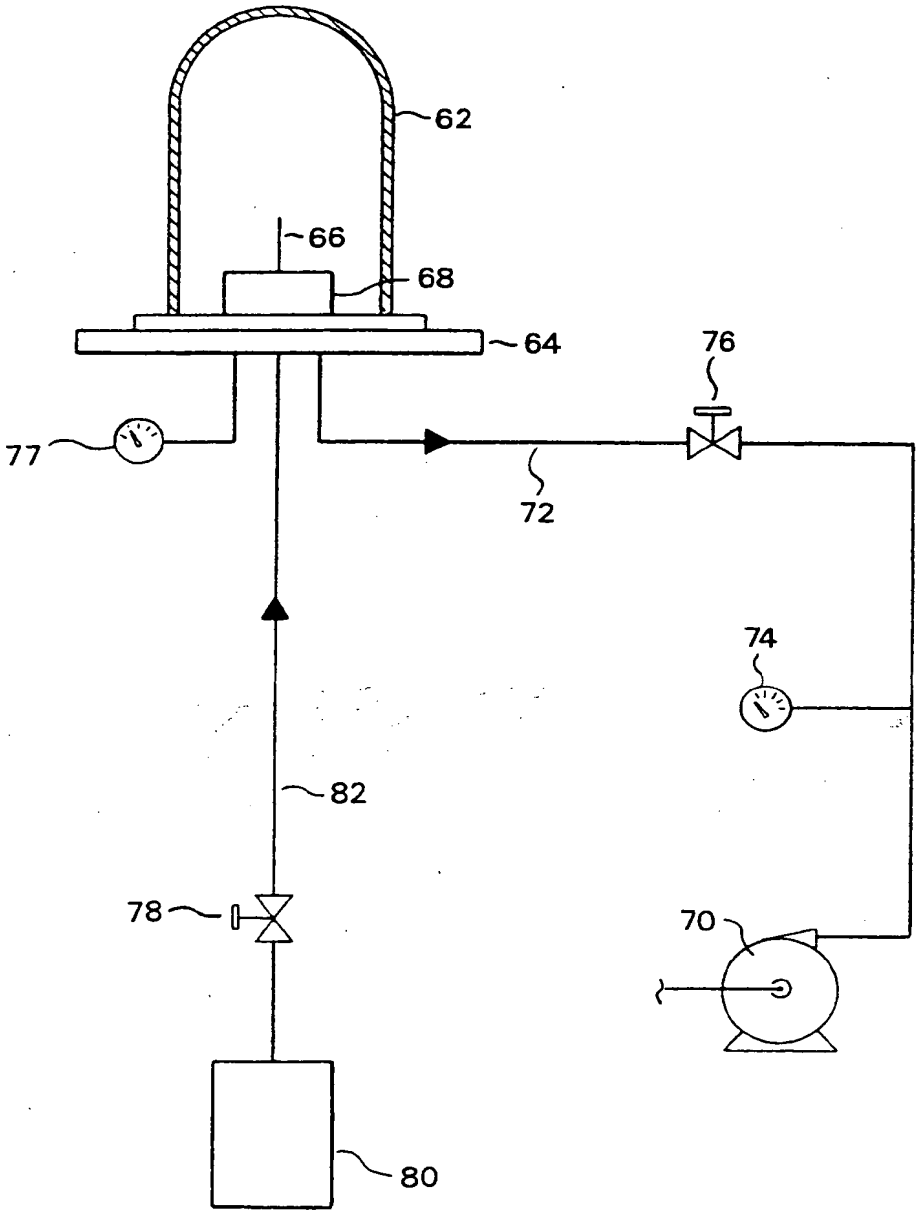


Fig 7



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EUROPEAN SEARCH REPORT

Application Number

EP 92 30 5950

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	PATENT ABSTRACTS OF JAPAN vol. 13, no. 137 (C-582)(3485) 5 April 1989 & JP-A-63 302 938 (DENKI KOGYO KK) 9 December 1988	1,2,8-10	C23C16/50 C23C16/26 H01Q19/00
Y		3-5,7,14	
A	* abstract *	6,11-13	
X	PATENT ABSTRACTS OF JAPAN vol. 13, no. 546 (C-661)(3894) 6 December 1989 & JP-A-1 222 054 (SUMITOMO ELECTRIC INDUSTRIES LTD) 5 September 1989	1,2	
A	* abstract *	3-14	
Y,D	US-A-4 434 188 (M. KAMO ET AL) * claims 1,2 *	3-5,7,14	
A	EP-A-0 106 698 (ENERGY CONVERSION DEVICES INC) * page 15, line 28 - line 32; figure 1 *	6	
A	PATENT ABSTRACTS OF JAPAN vol. 1, no. 117 (E)6 October 1977 & JP-A-52 050 143 (TOKIO SAKURAI) 21 April 1977 * abstract *	11-13	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C23C
H01Q

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23 SEPTEMBER 1992	EKHULT H.U.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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